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PROVISIONAL SPECIFICATION

Decomposition of Organic Peroxides

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torpichen Street, Edinburgh, 3, Scotland, BASIL VIVIAN ALLER, REGINALD HAROLD HALL 5 and RICHARD NORMAN LACEY, all British Subjects, and all of the Company's Research and Development Department, Great Burgh, Epsom, Surrey, do hereby declare the nature of this invention to be 10 as follows:—

This invention is for an improvement in and a process for the manufacture of phenol and acetone by the decomposition of isopropyl benzene hydroperoxide or 15 peroxide.

It has been shown by Hock and Lang (Ber. 1944, 77 B, p. 257) that when isopropylbenzene is subjected to the action of molecular oxygen with concurrent exposure to short wave irradiation isopropyl benzene peroxide is formed and that the free peroxide obtained by the treatment of the resulting reaction mixture with aqueous alkali solution and subsequent 20 acidification of the purified alkali metal salt, is decomposed by refluxing for 1½ hours with 10% aqueous sulphuric acid whereby phenol and acetone are produced. The yield of phenol obtained in this manner was 75% of the theoretical, while the amount of acetone, the vapours of which passed through the reflux condenser, was not determined quantitatively. Tests carried out on similar lines to those published, yielded about 60% acetone. The 25 said publication also mentions the formation as by-product of the reaction of appreciable amounts of a substance which the authors assume to be di-methyl phenyl carbinol.

Attempts to improve the yields by working with sulphuric acid of lower strength than that used by Hock and Lang so as to avoid secondary reactions were 30 unsuccessful; the yields were the same or even less.

It has now been discovered that the yield of phenol can be considerably improved by effecting the decomposition

of said peroxides by means of sulphuric acid of substantially greater strength than that used by Hock and Lang, i.e. in excess of 10%. When, however, the concentration of the acid used is more than 70%, considerable discolouration of the 45 reaction mixture occurs, indicating the occurrence of condensations.

According to this invention, therefore, the decomposition of isopropyl benzene peroxide is effected and phenol and acetone are produced by reacting said peroxide with sulphuric acid of a strength substantially more than 10% but not exceeding 70% preferably in concentrations of 50 between 25 and 60%.

Throughout this specification the expressions peroxide or isopropyl benzene peroxide are used to include the isopropyl benzene hydroperoxide.

It has been discovered, furthermore, 55 that the treatment of the peroxide with acid is with advantage carried out at lower temperatures than those hitherto used and that reaction temperatures between 40° and 80° C. give excellent results. By the 60 use of acids of concentrations exceeding 10% and preferably between 25 and 60% according to the invention the decomposition proceeds faster even at the lower temperatures, than with more dilute acids at 65 refluxing temperatures. The enhanced rate of decomposition of the peroxide makes it possible to reduce the size of the reaction vessel which offers the advantage of reducing at the same time the potential danger 70 inherent in heating large amounts of the peroxide. On the other hand, secondary reactions and, consequently, losses in the conversion into phenol and acetone are 75 minimised.

As the rate of the decomposition of the percompound depends on its concentration at any time the carrying out of the process in batches requires a long time and is therefore liable to side reactions. A preferred method, therefore, comprises effecting the process in a continuous manner whereby, also, the accumulation of large 80

amounts of percompounds in the reactor is avoided. This decomposition in a continuous manner may be carried out, for instance, by feeding the peroxide into dilute sulphuric acid of the specified concentration, e.g. of 25—60% at a temperature between 40° and 80° C. continuously or intermittently at about the same rate as it is decomposed, so that its concentration in the reaction mixture in the reactor does not exceed a low figure, say 2%, preferably even less, of the total weight. In order to facilitate the dosage and handling of the percompound it is preferable to add it in a diluted form for instance dissolved in an organic solvent inert towards the percompound and the sulphuric acid. A suitable solvent is e.g. isopropyl benzene, and therefore the reaction mixture resulting from the reaction of molecular oxygen upon liquid isopropyl benzene containing preferably from 10 to 40% isopropyl benzene peroxide may be used with advantage. As reactor may be used a vessel provided with an efficient agitator and a decanter which allows the continuous withdrawal of an oily layer containing, with small amounts of undecomposed percompound, the greater part of the phenol and acetone produced by the reaction whilst the volume of liquid in the agitator vessel comprising practically the whole of the aqueous acid remains constant. After reaching the steady state the whole of the phenol and acetone formed is thus withdrawn.

In place of one single agitator vessel a number of such vessels may be arranged in series. This makes it possible to use comparatively high concentrations of peroxide in the liquid mixture and thereby ensuring the highest reaction rates. By working in this way it is also possible to reduce the size of each individual vessel to a very large extent. The rate of reaction when working in a continuous manner was found to be several times greater than that attained in the case of the batch process. The explanation for this is not clear but it may be due to the fact that in the continuous process there is all the time a maximum amount of acetone present, part of which is dissolved in the aqueous sulphuric acid phase in which the actual decomposition of the percompound occurs. The presence of the acetone in the acid, on the other hand, increases the solubility therein of the peroxide whereby the reaction is facilitated and speeded up. This effect may be enhanced still further by recycling part of the recovered acetone to the reactor, thereby increasing the acetone content in the acid and, consequently, the solubility of the peroxide therein. The concentra-

tion of the acetone in the reaction mixture, however, should be kept sufficiently low to prevent complete miscibility of the two phases in the reactor and the formation of an homogeneous mixture, whereby the withdrawal from the reactor of an oily layer and the retention in the reactor of the aqueous acid phase would be obviated.

Another method of carrying out the process of the invention in a continuous manner comprises passing the aqueous sulphuric acid in conjunction with the peroxide preferably dissolved in a suitable solvent through a narrow tube at a velocity which is sufficiently high to cause turbulent flow and thereby achieve a good mixture. A mutual solvent such as acetone may be added to the reaction mixture. A limitation regarding the quantity of the added solvent is not necessary in this case, as part of the whole reaction mixture including the aqueous acid is withdrawn from the reactor tube.

Although it is known that acetone and phenol may condense under the influence of sulphuric acid, it is surprising that under the conditions in which the process of this invention is carried out no such condensation occurs. It is therefore an additional feature of the invention not to remove the acetone as soon as it is formed from the reaction mixture. Accordingly, it may be recovered for instance by distillation from the oil phase after the latter has been separated from the aqueous phase. The aqueous acid may then be returned to the reactor.

When solutions of peroxide in water-immiscible solvents such as are obtained, for instance, by treating isopropyl benzene with molecular oxygen, are treated according to this invention, it was found that the rate of decomposition increased with the volume ratio of the aqueous phase to the oil phase. It is, therefore, preferred to use in the reactor a phase ratio greater than one. This improvement allows the speeding up of the rate of flow through the reactor without impairing the rate of decomposition and offers thereby the advantage for the same output of further reducing the size of the reactor.

As the decomposition of the peroxide is strongly exothermic, cooling equipment should be provided for in order to keep the temperature in the reactor under proper control.

The oil layer leaving the reactor usually contains some sulphuric acid. This may be removed by washing with small amounts of water or aqueous acetone. The addition of small amounts of water to the oil before it is subjected to the dis-

tillation has also proved satisfactory. 8.9 gms. of acetone were obtained, i.e. yields of 83% and 65.5% respectively.

The following examples illustrate the manner in which the process of the invention may be carried out:—

EXAMPLE 1.

5 50 gms. of the sodium salt of isopropyl benzene hydroperoxide containing water of crystallisation and corresponding to 23.8 gms. isopropyl benzene peroxide 10 were added whilst stirring over a period of 10 minutes to 100 cc. of 60% w/v sulphuric acid at 60° C. When addition was complete the agitation was continued for a further 10 minutes. After shaking the 15 reaction liquid with some isopropyl benzene to take up the bulk of the phenol it was found that the oil phase contained 13.6 gms. phenol and 4.23 gms. acetone and the aqueous phase 1.12 gms. phenol 20 and 2.23 gms. acetone. The yield of phenol was thus quantitative, that of acetone 71%. When refluxing the sodium salt with the same volume of 10% sulphuric acid and distilling off the acetone 25 the yield of phenol was 72% and of acetone 58%, the time required for completion of the reaction being 2½ hours.

EXAMPLE 2.

30 A mixture of 160 cc. of a 55% w/v aqueous sulphuric acid and 160 cc. of a solution of 16.7% w/v isopropyl benzene peroxide in isopropyl benzene (resulting from the oxidation of isopropyl benzene) is thoroughly stirred and the temperature 35 maintained at 60° C. After 20 minutes 94.3 and after 30 minutes 98.2% of the peroxide initially present had been decomposed. During the reaction and for some time afterwards a stream of nitrogen was 40 passed through the liquid in order to remove the acetone formed. Phenol was obtained in a yield of 91.3%, acetone of 86.5%.

EXAMPLE 3.

45 To 100 cc. 55% w/v sulphuric acid which were refluxed 100 cc. 35.6% w/v isopropyl benzene peroxide solution in isopropyl benzene were added over a period of 10 minutes acetone being removed as 50 formed through a short column. The mixture was boiled for a further 5 minutes. 18.22 gms. of phenol and

EXAMPLE 4.

55 In a vessel provided with a stirrer a mixture of 150 cc. of 55% w/v sulphuric acid and 138 cc. of an oxidation solution, consisting of 44.5 gms. isopropyl benzene peroxide in 100 cc. of isopropyl benzene 60 were kept at 60° C. for 15 minutes, whereupon continuous feeding of the same isopropyl benzene solution was started while at the same time through a decanter a corresponding volume of oil layer over 65 flowed. After the conditions became steady, 787 cc. of oil, containing 193 gms. phenol and 115 gms. acetone were collected over a period of 5 hours, while over the same period 770 cc. of the peroxide 70 solution were fed into the vessel. The yield of phenol was thus 91.4%, of acetone 88%, based on the total peroxide fed, whilst 3.6% of the initially fed peroxide were undecomposed. Of the oil which 75 contained 14.55% w/v acetone and 24.5% w/v phenol, the acetone was recovered by distillation after the adhering sulphuric acid was diluted by addition of some 80 water.

EXAMPLE 5.

To 100 cc. of a mixture of equal volumes of ethanol and water and containing 14.1 gms. sulphuric acid 10.1 gms. of isopropyl benzene peroxide were added 85 and the homogeneous mixture kept at 70° C. After 50 minutes 94% of the initial percompound had reacted. At that time 5.75 gms. of phenol were obtained from the solution which corresponds to 90 92% of the initially added peroxide.

The process of the invention is applicable also to the production of phenol derivatives by the decomposition of peroxide compounds of a similar nature, that 95 is of peroxides of benzene derivatives in which the substituents are one or more alkyl groups and at least one of which has a tertiary carbon atom in the alpha position to the benzene ring, and the production thereby of phenol derivatives and ketones.

Dated this 18th day of August, 1947.

N. F. BAKER.
Agent for the Applicants.

COMPLETE SPECIFICATION

Decomposition of Organic Peroxides

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torpichen 105 Street, Edinburgh, 3, Scotland, BASIL VIVIAN ALLER, a British Subject, REGINALD HAROLD HALL, a British Subject, and RICHARD NORMAN LACEY, a British Subject, all of the Company's

Research and Development Department, 110 Great Burgh, Epsom, Surrey, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following 115 statement:—

BAD ORIGINAL

This invention is for an improvement in and a process for the decomposition of the hydroperoxides of lower alkyl benzenes wherein the peroxide group is linked to an aliphatic tertiary carbon atom attached to the benzene ring, and the manufacture thereby of phenol and ketones.

It has been shown by Hock and Lang 10 (Ber. 1944, 77 B, p. 257) that when isopropylbenzene is subjected to the action of molecular oxygen with concurrent exposure to short wave irradiation isopropylbenzene hydroperoxide is formed 15 and that the free hydroperoxide obtained by the treatment of the resulting reaction mixture with aqueous alkali solution and subsequent acidification of the purified alkali metal salt, is decomposed by refluxing for 1½ hours with 10% aqueous sulphuric acid whereby phenol and acetone are produced. The yield of phenol obtained in this manner was 75% of the theoretical, while the amount of acetone, 20 the vapours of which passed through the reflux condenser, was not determined quantitatively. Tests carried out on similar lines to those published, yielded about 60% acetone. The said publication 25 also mentions the formation as by product of the reaction of appreciable amounts of a substance which the authors assume to be dimethyl phenyl carbinol.

Attempts to improve the yields by working with sulphuric acid of lower strength than that used by Hock and Lang so as to avoid secondary reactions were unsuccessful; the yields were the same or even less.

It has now been discovered that 30 the yield of phenol and ketones can be considerably improved by effecting the decomposition of hydroperoxides of alkyl benzenes with a tertiary carbon atom linked to the benzene ring by means of 35 aqueous sulphuric acid of substantially greater strength than that used by Hock and Lang, i.e. in excess of 10%. When, however, the concentration of the acid used is more than 70% the very considerable discolouration of the reaction mixture indicates an undesirable extent of condensation of the various decomposition products.

Alkyl benzene hydroperoxides of the 40 defined kind are for instance the hydroperoxides of isopropyl-benzene, secondary butyl benzene and *p*-cymene, but it is to be understood that the process of this invention is not restricted to these 45 compounds.

Throughout this specification the expression "peroxide" and "percompound" is used to include the hydroperoxide.

50 The percentages given in this specifica-

tion and in the appended claims are in parts by weight per hundred parts by volume, and the temperatures are given in Centigrade. In this connection, the parts by weight bear the same relation to parts by volume as do grams to cubic centimeters.

According to this invention, therefore 55 the decomposition of hydroperoxides of alkyl benzenes, in which the peroxide group is linked to an aliphatic tertiary carbon atom attached to the benzene ring and the alkyl groups do not contain more than five carbon atoms is effected, and phenol and ketones are produced by reacting 60 said peroxides with aqueous sulphuric acid of a strength substantially more than 10% but not exceeding 70% preferably in concentrations of between 25 and 60% and at elevated temperatures. 65

It has been discovered furthermore that 70 the treatment of the peroxide with acid is with advantage carried out at lower temperatures than those hitherto used and that reaction temperatures up to 80°, preferably between 40 and 80° C., give 75 excellent results.

By the use of aqueous sulphuric acid of 80 concentrations exceeding 10% and preferably between 25 and 60% according to 85 the invention, the decomposition proceeds faster even when effected at the lower temperatures than with more dilute acids at refluxing temperatures. The enhanced rate of decomposition of the peroxides 90 makes it possible to reduce the size of the reaction vessel which offers the advantage of reducing, at the same time, the potential danger inherent in heating large 95 amounts of peroxides. On the other hand, 100 secondary reactions and, consequently, losses in the conversion into phenol and acetone are minimised. As the rate of the decomposition of the peroxides depends on their concentration at any 105 time the carrying out of the process in batches requires a long time and is, therefore, liable to side reactions. A preferred method, therefore, comprises effecting the 110 process in a continuous manner, whereby, 115 also, the accumulation of large amounts of percompounds in the reactor is avoided. This decomposition in the continuous manner may be carried out, for instance, by feeding the peroxides 120 into dilute aqueous sulphuric acid of the specified concentration, e.g. of 25 to 60%, at a temperature between 40° and 80° continuously or intermittently at about 125 the same rate as they are decomposed, so that their concentration in the reaction mixture in the reactor or the reactors does not exceed a low figure, say 2%, preferably even less, of their initial weight. In order to facilitate the dosage and 130

handling of the percompounds, it is preferable to add them in a dissolved form, for instance dissolved in an organic solvent inert towards the percompound and the sulphuric acid. A suitable solvent in the case of isopropylbenzene hydroperoxide is, for instance, isopropylbenzene, and, therefore, the reaction mixture resulting from the reaction of molecular oxygen upon liquid isopropylbenzene at temperatures up to 150° and in the absence of catalysts other than peroxides and containing preferably from 10 to 45% of isopropylbenzene hydroperoxide may be used with advantage. As reactor may be used a vessel provided with an efficient agitator and attached thereto a device such as a decanter which allows the continuous separation and withdrawal of the lighter oily layer containing, with small amounts of other decomposition compounds, the greater part of the phenol and acetone produced by the reaction, whilst the heavier aqueous acid separated in the decanter is returned to the agitator vessel wherein the bulk is retained so that its volume remains practically constant. After reaching the steady state practically the whole of the phenol and acetone formed is thus withdrawn.

In place of one single agitator vessel, a number of such vessels may be arranged in series or cascades so that the separated oily phase flows or is pumped to the next subsequent vessel. This makes it possible to use comparatively high concentrations of peroxide in the liquid mixture in the first of the reaction vessels of a series thereby ensuring the highest reaction rates. By working in this way it is also possible to greatly reduce the size of each individual vessel. The rate of reaction when working in a continuous manner was found to be several times greater than that attained in the case of the batch process. The explanation for this is not clear but it may be due to the fact that in the continuous process there is all the time a maximum amount of ketone present, in the case of isopropylbenzene hydroperoxide for instance acetone, part of which is dissolved in the aqueous sulphuric acid phase in which the actual decomposition of the percompounds occurs. The presence of this ketone in the acid, on the other hand, increases the solubility therein of the peroxides, whereby the reaction is facilitated and speeded up. This effect may be enhanced still further by recycling a part of the recovered ketone to the reactor or adding fresh ketone thereto, thereby increasing the ketone contained in the acid and consequently the solubility of the peroxide. The concentration of the ketone in the

reaction mixture, however, should be kept sufficiently low to prevent complete miscibility of the two phases in the reactor and the formation of a homogeneous mixture, whereby the withdrawal from the reactor or the reactors of an oily layer and the retention in the reactor or reactors of the aqueous acid phase would be obviated.

Another method of carrying out the process of the invention in a continuous manner comprises passing the aqueous sulphuric acid in conjunction with the peroxide, preferably dissolved in a suitable solvent which is immiscible with the aqueous acid and not attacked by the components of the reaction mixture, such as benzene, toluene and xylene, preferably the alkyl benzenes which were the starting material for the peroxide production, through a narrow tube at a velocity which is sufficiently high to cause turbulent flow and thereby achieve a good mixture. A mutual solvent which is inert to the reaction mixture under the conditions of the reaction, may be added to the reaction mixture. Such solvents are for instance ketones like acetone and alcohols like ethanol. A limitation regarding the quantity of the added mutual solvent is not necessary in this case, as part of the whole reaction mixture, including the aqueous acid is withdrawn from the reactor tube. The use of a reactor tube, however, offers special advantages only, when the reaction mixture is heterogeneous.

The working in a homogeneous phase by the addition of a mutual solvent is advantageous also when the process of the invention is carried out in a batchwise manner. Suitable solvents are such alcohols, ketones and ethers of low molecular weight which are completely miscible with water. Alcohols of this nature are for instance methanol, propanol, isopropanol, tertiary butanol; ketones are acetone, methyl ethyl ketone; and ethers for instance ethers of ethylene glycol and di-ethylene glycol; furthermore dioxane.

Although it is known that ketones, for instance acetone, and phenol, may condense under the influence of sulphuric acid at elevated temperatures, it is surprising that under the conditions in which the process of this invention is carried out practically no such condensation occurs. It is, therefore, an additional feature of the invention not to remove the ketone as soon as it is formed from the reaction mixture. Accordingly, it may be recovered, for instance, by distillation, from the oil phase after the latter has been separated from the aqueous phase.

The aqueous acid may then be returned to the reactor.

When solutions of hydroperoxides in water-immiscible solvent such as are obtained for instance by treating isopropylbenzene with molecular oxygen at elevated temperatures in the substantial absence of oxidation catalysts other than peroxides were treated according to this invention, it was found that the rate of decomposition increased with the volume ratio of the aqueous acid phase to the oil phase. It is, therefore, preferred to use in the reactor or reactors an initial phase ratio greater than one. The upper limit for the volume of aqueous acid used is governed by economical considerations. This improvement allows the speeding up of the rate of flow through the reactor without reducing the extent of decomposition and offers thereby the advantage for the same output of further reducing the size of the reactor.

As the decomposition of the peroxide is strongly exothermic, cooling equipment should be provided in order to keep the temperature in the reactor or reactors under proper control.

The non-aqueous oil layer leaving the reactor usually contains some sulphuric acid. This may be removed by washing with small amounts of water or aqueous ketones whereupon the oil layer is worked up for the reaction products. The ketones and phenol may be recovered therefrom, for instance by subjecting the oil phase to distillation, whereby the ketones are distilled off. The residue from the distillation is distilled *in vacuo*, which removes the solvent, for instance, isopropylbenzene, and any methyl styrene formed as a by product during the reaction. The residue from this last distillation is fractionated in a third still under vacuum and the distillate is condensed at about 50° C. On cooling the phenol crystallises in a state of high purity and with a good melting point.

50 The following examples illustrate the manner in which the process of the invention may be carried out.

EXAMPLE 1.

55 50 grams of the sodium salt of isopropylbenzene hydroperoxide containing water of crystallisation and corresponding to 23.8 grams of isopropyl benzene hydroperoxide were added whilst stirring over a period of 10 minutes to 100 cc. of 60% aqueous sulphuric acid at 60°. When addition was complete the agitation was continued for a further 10 minutes.

After shaking the reaction liquid with some isopropyl benzene to take up the

bulk of the phenol it was found that the oil phase contained 13.6 grams of phenol and 4.23 grams of acetone and the aqueous phase 1.12 grams of phenol and 2.23 grams of acetone. The yield of phenol was thus quantitative, that of acetone 71%. When refluxing the sodium salt with the same volume of 10% aqueous sulphuric acid and distilling off the acetone the yield of phenol was 72% and of acetone 58%, the time required for completion of the reaction being 2½ hours.

EXAMPLE 2.

A mixture of 160 cc. of a 55% aqueous sulphuric acid and 160 cc. of a solution of 16.7% isopropyl benzene peroxide in isopropyl benzene (resulting from the oxidation of isopropyl benzene) was thoroughly stirred and the temperature maintained at 60°. After 20 minutes 94.3% and after 30 minutes 98.2% of the peroxide initially present had been decomposed. During the reaction and for some time afterwards a stream of nitrogen was passed through the liquid in order to remove the acetone formed. Phenol was obtained in a yield of 91.3%, acetone of 86.5%.

A similar run showing the deleterious influence of higher temperatures gave the following result:

To 100 cc. 55% aqueous sulphuric acid which were refluxed 100 cc. of 35.6% isopropyl benzene hydroperoxide solution in unreacted isopropyl benzene were added over a period of 10 minutes, acetone being removed as formed through a short column. The mixture was boiled for a further 5 minutes. 18.22 grams of phenol and 8.9 grams of acetone were obtained, i.e. yields of 83% and 65.6% respectively.

EXAMPLE 3.

In a vessel provided with a stirrer a mixture of 150 cc. of 55% aqueous sulphuric acid and 138 cc. of an oxidation mixture containing 44.5 grams of iso-propyl benzene hydroperoxide in 100 cc. of said oxidation mixture were kept at 60° for 15 minutes, whereupon continuous feeding of the same isopropyl benzene hydroperoxide solution was started while at the same time a corresponding volume of oil layer overflowed through a decanting device which separates and withdraws continuously the lighter oil phase from the heavier aqueous acid. After the conditions became steady, 787 cc. of oil, containing 193 grams of phenol and 115 grams of acetone were collected over a period of 5 hours, while over the same period 77 cc. of the peroxide solution were fed into the vessel. The yield of phenol was thus 91.4% and acetone 88%, based

on the total peroxide fed, whilst 3.6% of the initially fed peroxide was undecomposed. From the oil which contained 14.55% acetone and 24.5% phenol, the acetone was recovered by distillation after diluting the adhering sulphuric acid by addition of water.

EXAMPLE 4.

To 100 cc. of a mixture of equal volumes of ethanol and water and containing 14.1 grams of sulphuric acid 10.1 grams of isopropyl benzene hydroperoxide were added and the homogeneous mixture kept at 70°. After 50 minutes 94% of the initial percompound had reacted. At this time 5.75 grams of phenol were obtained from the solution which corresponds to a yield of 92% based on the initially added peroxide, or 98% based on the peroxide decomposed.

EXAMPLE 5.

160 cc. of a solution of isopropyl benzene hydroperoxide in isopropyl benzene and containing 20.6 grams of the peroxide in 100 cc. of the solution were agitated with 160 cc. of 25% aqueous sulphuric acid at 70° in a water bath. The decomposition of the peroxide was practically complete after 3 hours and amounted to 96.3%. The yield of phenol resulting from the decomposition and based on the peroxide decomposed was 83.7% and that of acetone was 76.3%.

EXAMPLE 6.

10 grams of secondary butyl benzene hydroperoxide were mixed with 50 cc. of aqueous sulphuric acid of 25% strength and heated for two hours at 65° C.

The reaction mixture was extracted with ether and the extract distilled.

Fraction 1	70—80°	1 gram
Fraction 2	80—165°	0.6 "
Fraction 3	165—185°	5.8 "
Residue	- - -	0.3 "

The greater part of Fraction 3 proved to be phenol, thus showing that the yield was almost theoretical.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:

1. Process for the decomposition of alkyl benzene hydroperoxides in which the peroxide group is linked to an aliphatic tertiary carbon atom attached to the benzene ring and the alkyl groups do not contain more than 5 carbon atoms, is effected and phenol and ketones are produced by reacting said peroxides at elevated temperatures with aqueous sulphuric acid of strength substantially

more than 10% but not exceeding 70% weight/volume.

2. Process according to claim 1, wherein the temperature does not exceed 80° C. and is preferably between 40 and 80° C.

3. Process according to claim 1 or 2, wherein the acid strength is between 25 and 60%.

4. Process according to claim 1, 2 or 3, wherein the peroxides dissolved in a water-immiscible inert solvent are brought into contact with the acid.

5. Process according to claim 4, wherein the volume ratio of the aqueous acid phase to the oil phase in the reactor is greater than one.

6. Process according to claims 4 or 5, wherein a solvent for all the components of the reaction mixture is added thereto.

7. Process according to claim 6, wherein the amount of the added solvent for all the components is such that the reaction mixture is homogeneous.

8. Continuous process according to any of claims 4, 5 or 6 which comprises separating from the aqueous acid phase the oil phase partly or completely after the desired extent of decomposition has been achieved therein, recovering from the separated amount of the oil phase the phenol and ketone contained therein and adding fresh peroxide solution to the remaining part of the reaction mixture without removing therefrom the ketone dissolved therein.

9. Process according to any of the preceding claims, wherein the peroxide is isopropyl benzene hydroperoxide.

10. Process according to claim 9, wherein the isopropylbenzene hydroperoxide is dissolved in isopropyl benzene.

11. Process according to claim 10, wherein the solution of isopropyl benzene hydroperoxide in isopropylbenzene is the reaction mixture resulting from the oxidation of isopropylbenzene with molecular oxygen-containing gases at elevated temperatures in the absence of oxidation catalysts other than peroxides.

12. Process according to any of the preceding claims, wherein the reaction is carried out in the presence of added ketone.

13. Process according to claim 12, wherein acetone is added to the reaction mixture.

14. Process according to claim 12, wherein methyl ethyl ketone is added to the reaction mixture.

15. Process according to any of the preceding claims 1 to 8, wherein the peroxide is secondary butyl benzene hydroperoxide.

16. Process substantially as described in any of the examples 1 to 6.

17. Phenol and ketones when produced by a process as claimed in any of the claims 1 to 16.

Dated this 17th day of August, 1948.
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. Agent for the Applicants.

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